Continuous-Fiber Ceramic Composites (CFCCs) For Industrial Gas Turbines

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CFCC

CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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The CFCC Program at ORNL Has Evolved Over The Past Few Years → Two Primary Areas Of Focus

- Understand the deleterious effects of water vapor on Si-based materials (Environmental Effects Task)
  - *Laboratory exposures of standard materials to high H_2O pressures (>1atm)*
  - *corrosion analysis of exposed standards*
- Collaborate with industry on the development and implementation of CFCC combustor liners for gas turbines (Composite Characterization Task)
  - *laboratory exposures of candidate materials to simulated combustion environments*
  - *extensive microstructural characterization*
  - *mechanical evaluation of exposed materials*

Environmental Effects Effort Addresses Oxidation Of Si-Based Materials At High H_2O Pressures (> 1 atm)

- Effects of H_2O on materials degradation is of increasing concern as stationary gas turbine and microturbine technology moves toward higher temperatures, higher pressure ratios, and NO_x control
  - Substantially accelerated rates of SiC oxidation observed at higher H_2O pressures even at low gas velocity
  - Studies conducted at water-vapor pressures relevant to combustion environments in gas turbines

Results from this effort have been used to develop a fundamental understanding of the degradation of SiC, Si, and SiC-based CFCCs in gas turbine combustion environments

There Are Several Approaches For Evaluating High-Temperature Environmental Effects

- Static atmosphere furnaces

- Slow-flow (< 1 fps) systems
  - *microbalances*
  - *tube furnaces (atm. pressure)*
  - *high-pressure systems (ORNL's Keiser Rig)*

- Intermediate-velocity systems (10^2 fps, combustor liners)
  - *atmospheric burner rigs*
  - *high-pressure rigs (NASA, GE, etc.)*

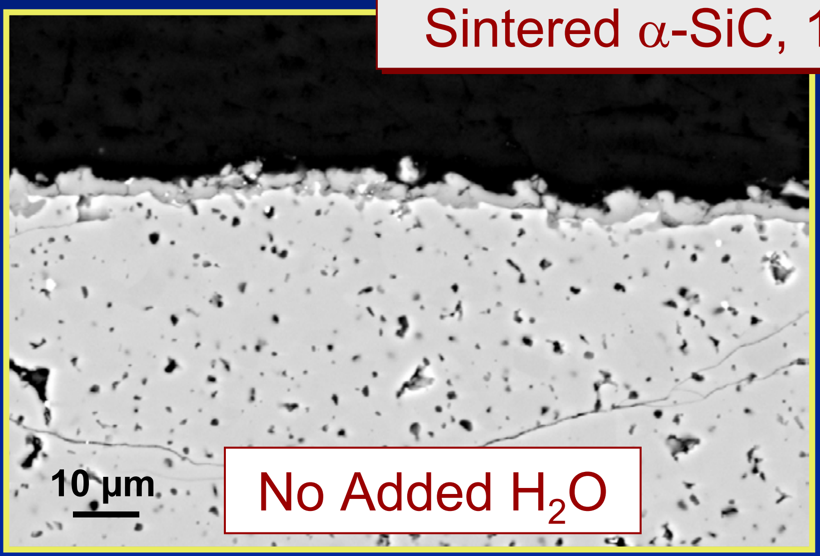
- High-velocity systems (~10^3 fps, nozzles, blades, vanes)
  - *currently being built at Honeywell*

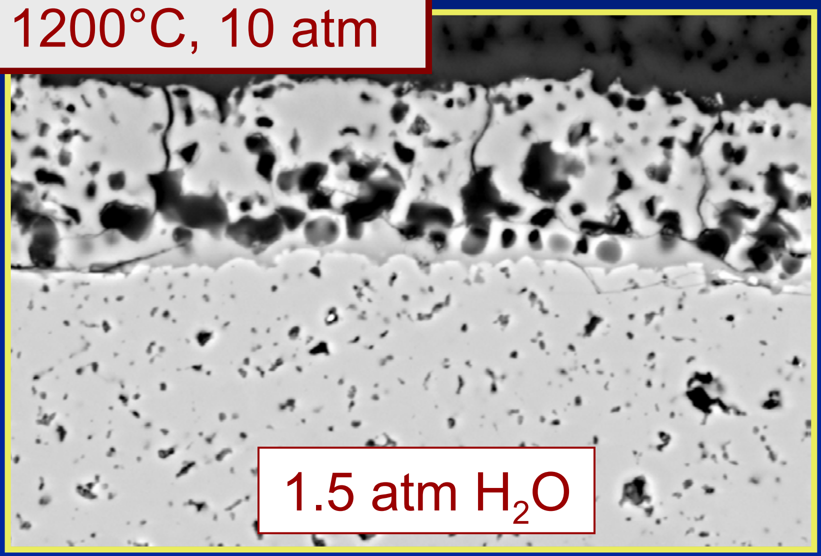
At Higher Pressures Of Water Vapor (>1 atm), Oxidative Degradation Is Significant

Recent work on monolithic SiC, Si_3N_4:

- Effects on parabolic rate constant (Opila, J. Am. Ceram. Soc.,1999)
- SiO_2 volatility (Opila & Jacobson, ECS Proc.1997; Opila & Hann, J. Am. Ceram. Soc., 1997; Robinson & Smialek, J. Am. Ceram. Soc.,1999; Opila et al., J. Am. Ceram. Soc.,1999)
- Accelerated oxidation with nonprotective SiO_2 formation (More et al., J. Am. Ceram. Soc., 2000)

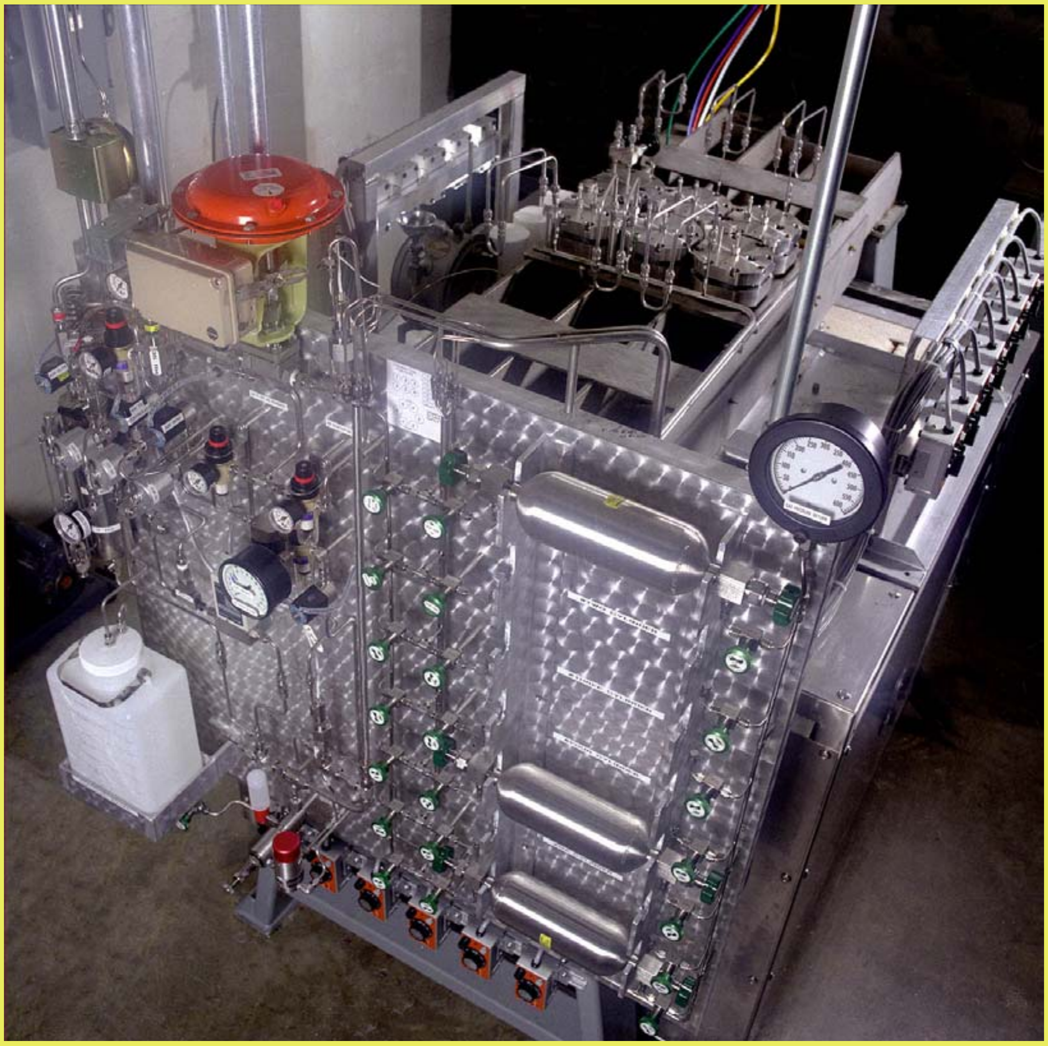
Sintered α-SiC, 100 h, 1200°C, 10 atm





Little effort on SiC-based composites (More et al., IGTI Proc., 1999)

High-Pressure Exposures Are Conducted In A Specialized High-Temperature Rig - *ORNL's Keiser Rig*



Both "standard" monolithics and relevant CFCCs have been exposed under simulated combustion conditions

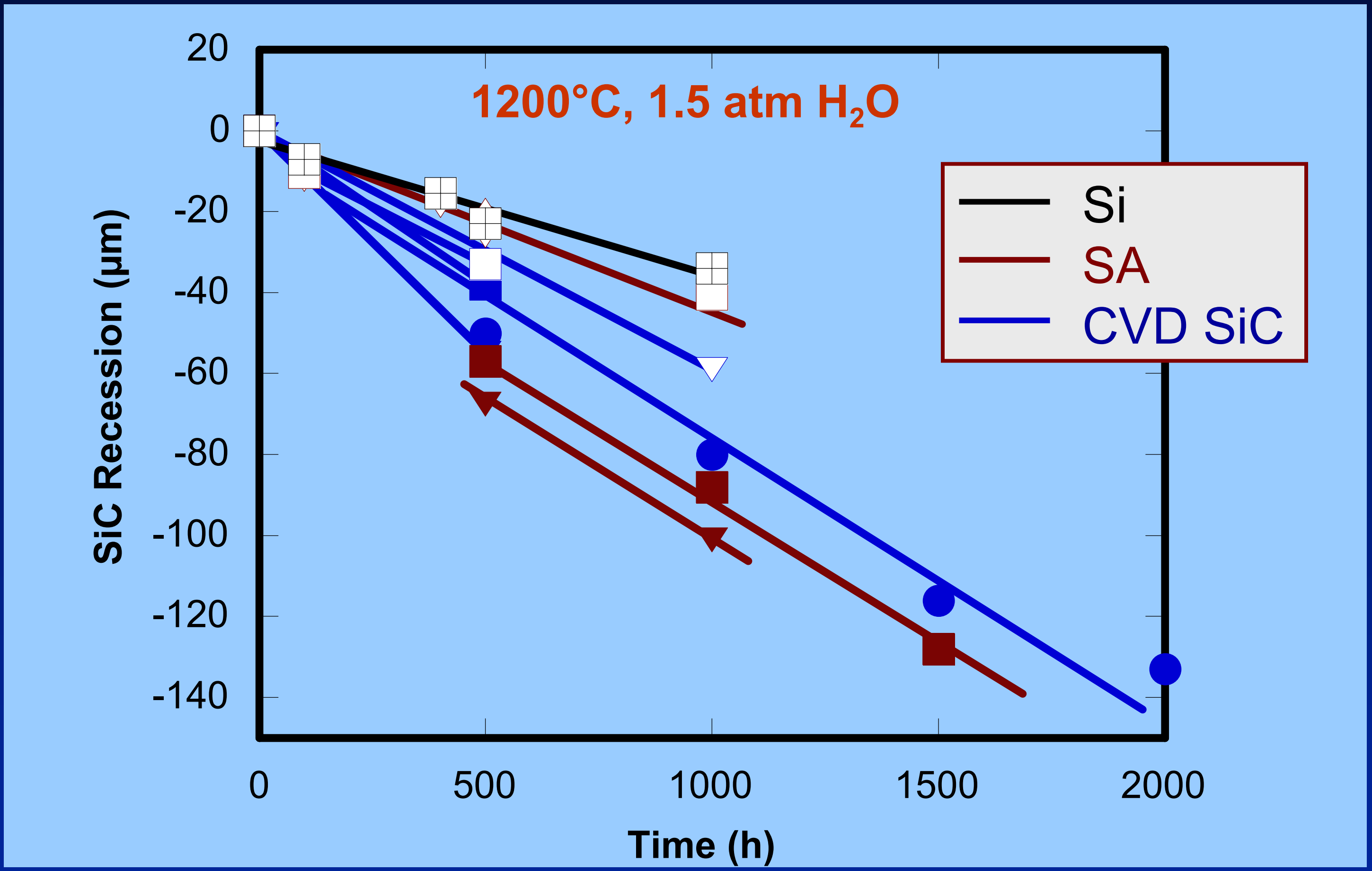
Exposures

- *1200°C*
- *H_2O pressure of 1.5atm at 10atm total pressure, balance air*
- *Low gas velocities (~100 cc/min)*

Materials

- *CVD SiC*
- *Sintered α (Hexoloy SA)*
- *Si - high purity*
- *MI- and CVI-processed CFCCs*

Recession Rate For Silicon Was High, But Lower Than That Of SiC (Both Are CFCC Constituents)



Si: 0.02 - 0.03 µm/h
SiC: 0.04 - 0.10 µm/h

CFCC Combustor Liner Project Is A Multi-Program Effort

- CSGT Program team is led by Solar Turbines and includes CFCC, coating manufacturers and industrial co-generation end users
  - *Supports component design, procurement, and testing*

- CFCC Program supports the Composite Characterization and Environmental Effects efforts at ORNL
  - *Microstructural and mechanical evaluation of engine-tested liners*
  - *Exposure of candidate CFCCs in Keiser Rig and subsequent characterization*

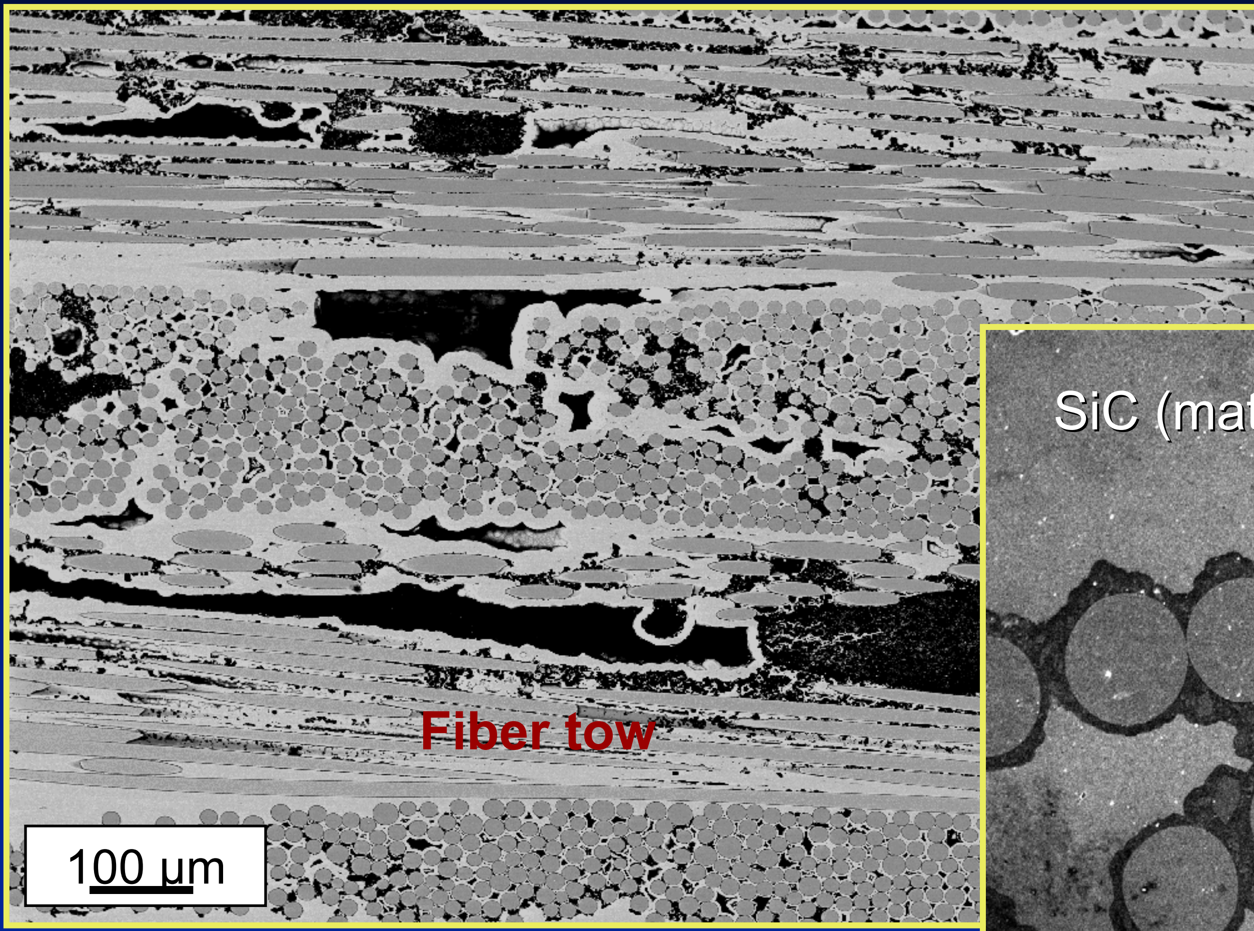
CSGT and CFCC Programs Represent Collaboration Between Industry and National Labs

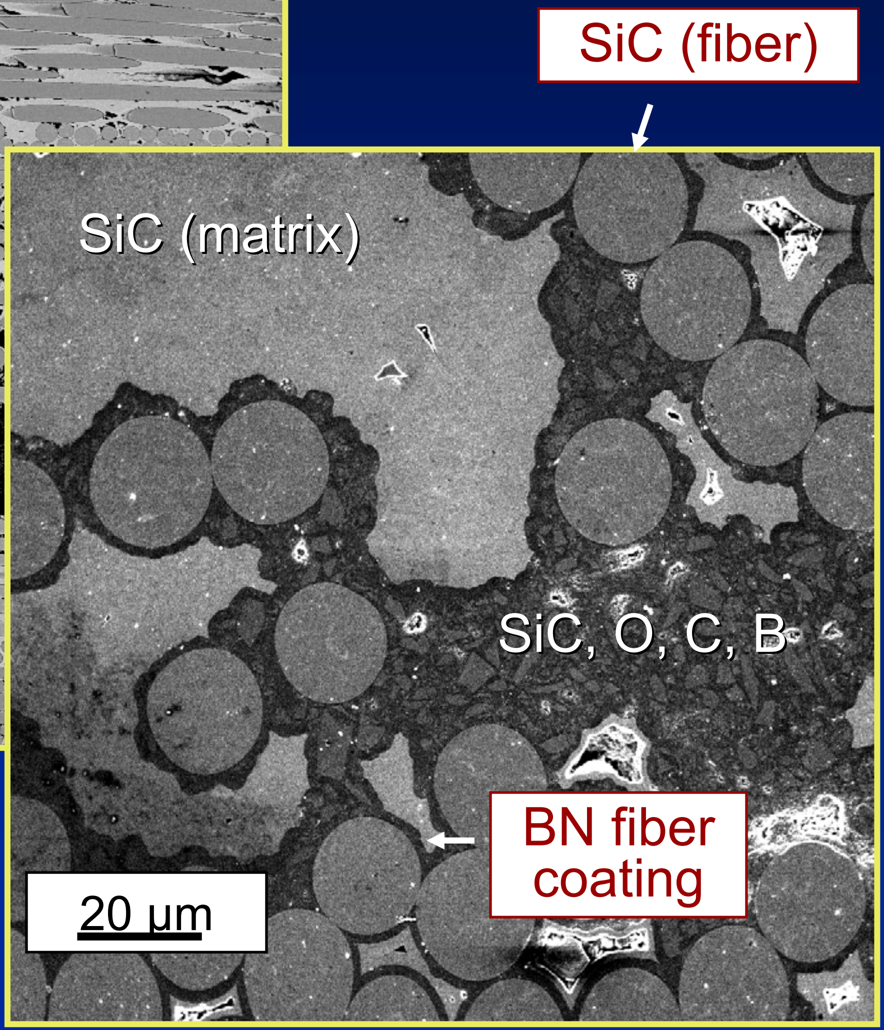
- Solar Turbines, Inc.
  - *Chevron Test Site, Bakersfield, CA*
  - *Malden Mills Co-Generation Site, Malden, MA*
- CFCC manufacturers
  - *GE Power Systems Composites, Inc.*
  - *B.F. Goodrich, Inc.*
- United Technologies Research Center
  - *EBC development and application*
- Oak Ridge National Laboratory
  - *Laboratory exposures*
  - *Microstructural and mechanical evaluation*
- Argonne National Laboratory
  - *NDE*

Evaluating CFCCs For Gas Turbine Environments $\rightarrow$ Several Primary Goals

- Characterizing degradation processes for representative environments *(high-temperature, high-H_2O pressures, <u>actual engine exposures</u>)*
- Establishing relationships between reactions and effects *(accelerated oxidation of SiC, borosilicate glass formation, <u>composite recession/consumption</u>)*
- Defining appropriate methodologies *(microstructural characterization of composite oxidation/damage, evaluation of protective coatings, <u>relevance of Keiser Rig exposures</u>)*
- Investigating better approaches to minimizing environmental effects by composite design, component selection, and coatings *(stable constituents and morphologies)*

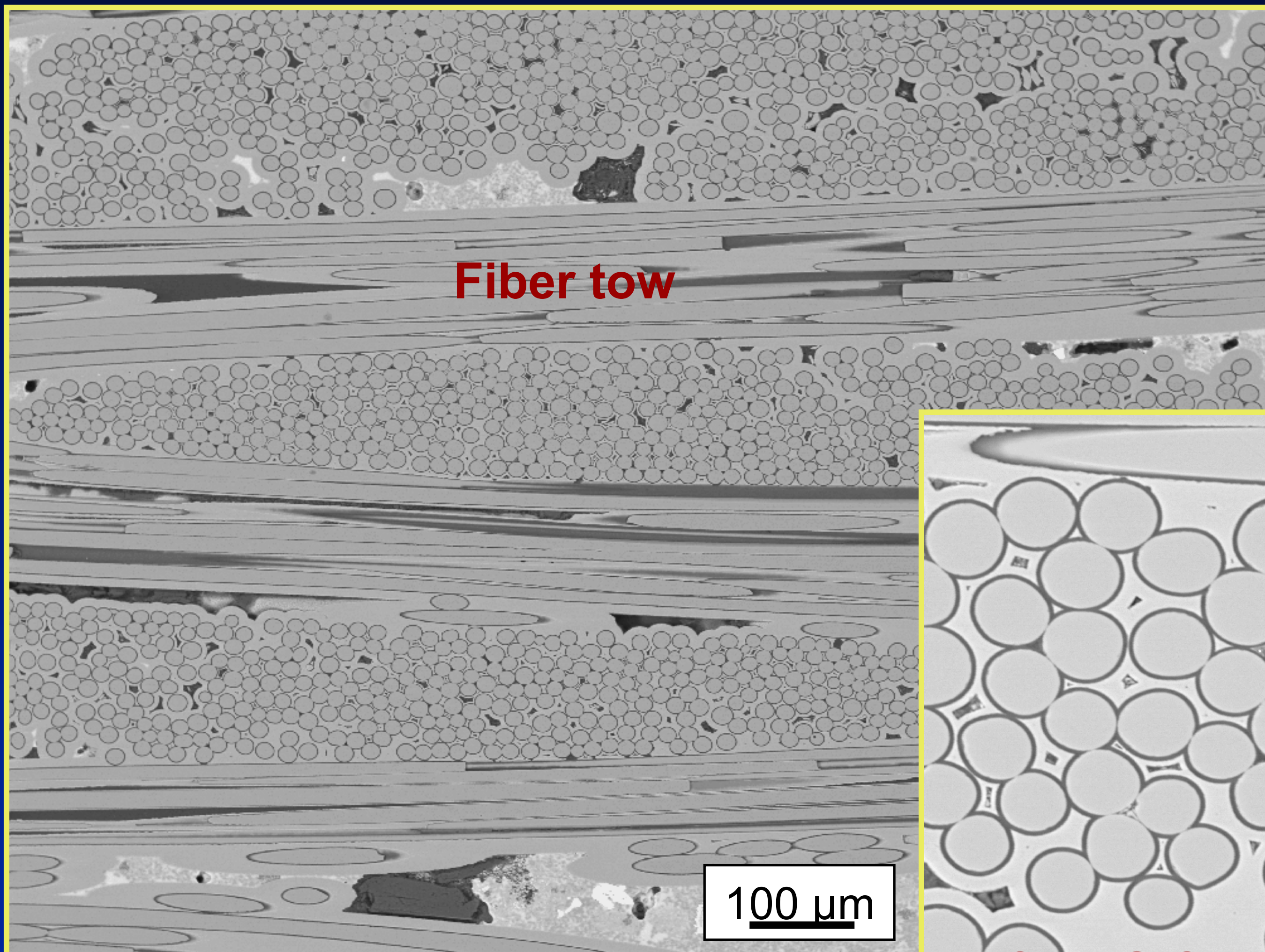
Two Types Of CFCC Materials Were Evaluated: (1) Chemical Vapor Infiltrated (CVI) SiC/BN/SiC



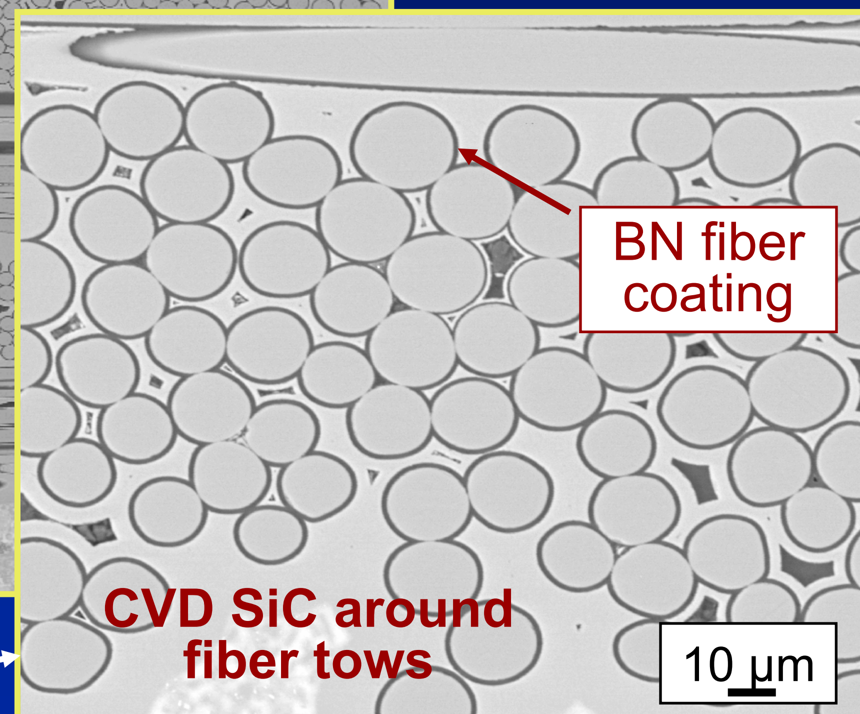


- B-containing filler
- no free Si in matrix

Two Types Of CFCC Materials Were Evaluated: (2) Melt-Infiltrated (MI) SiC/BN/SiC



Si+SiC composite matrix



BN fiber coating

SiC fiber

CFCC Recession/Degradation Depends On Composite Constituent Reactions With Environment

- CFCC constituents include:
  - Hi-Nicalon (SiC) fibers
  - BN interface coatings
  - CVD SiC around fibers
  - Si+SiC MI matrix (plus other impurities/additives)
  - Other B-containing phases in matrix
- Recession/damage accumulation will depend on the amounts of each constituent and how they react/interact in combustor environment

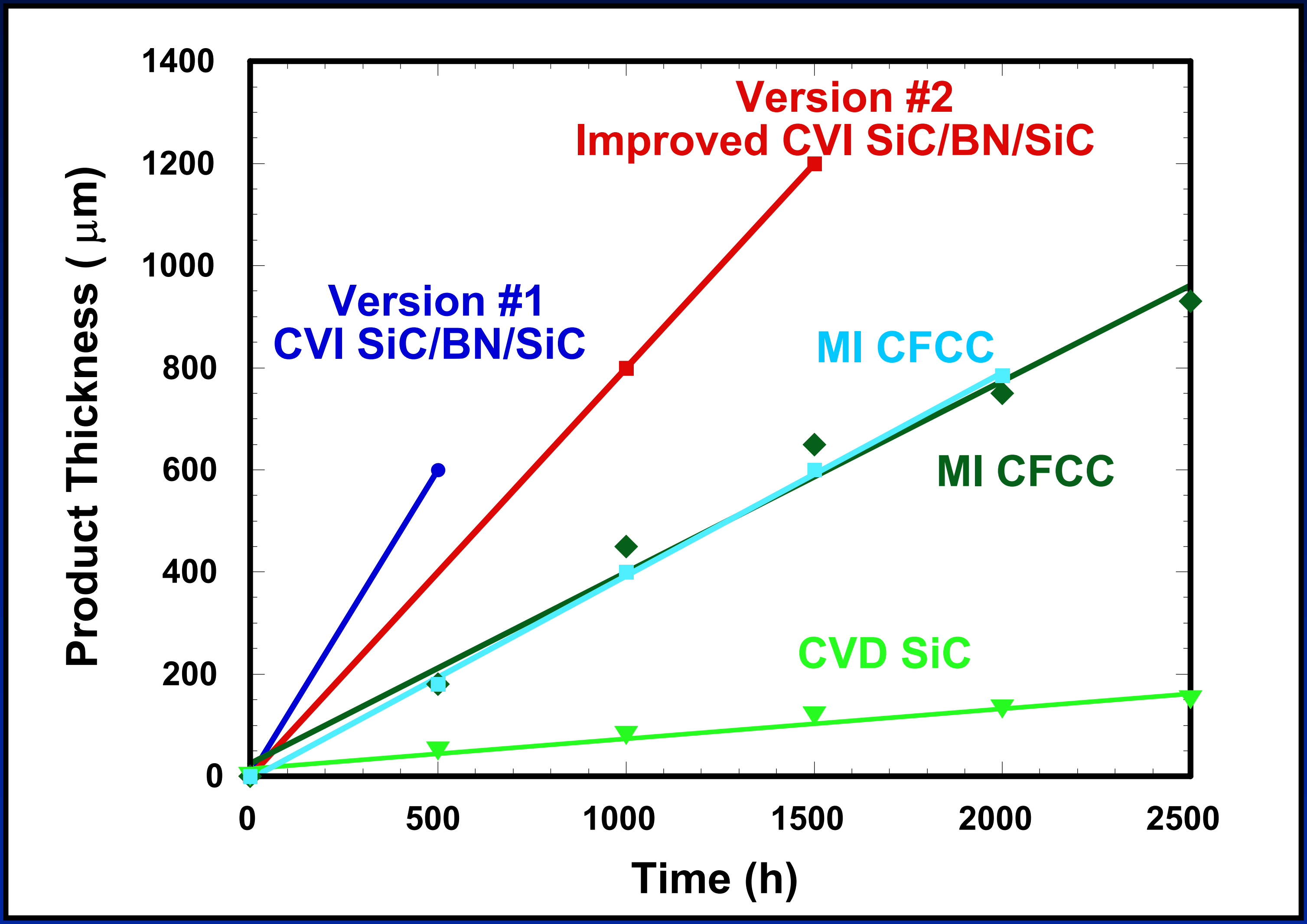
$Si + O_2 = SiO_2$
$SiC + 1.5O_2 = SiO_2 + CO$
$2BN + 3/2O_2 = B_2O_3 + N_2$
$SiO_2 + B_2O_3 =$ borosilicate glass

→

Plus all reactions of the solids with water vapor producing additional volatile products!

High Rates Of CFCC Oxidative Degradation/Recession Were Measured After Exposure In Keiser Rig

1200°C, 1.5 atm H_2O

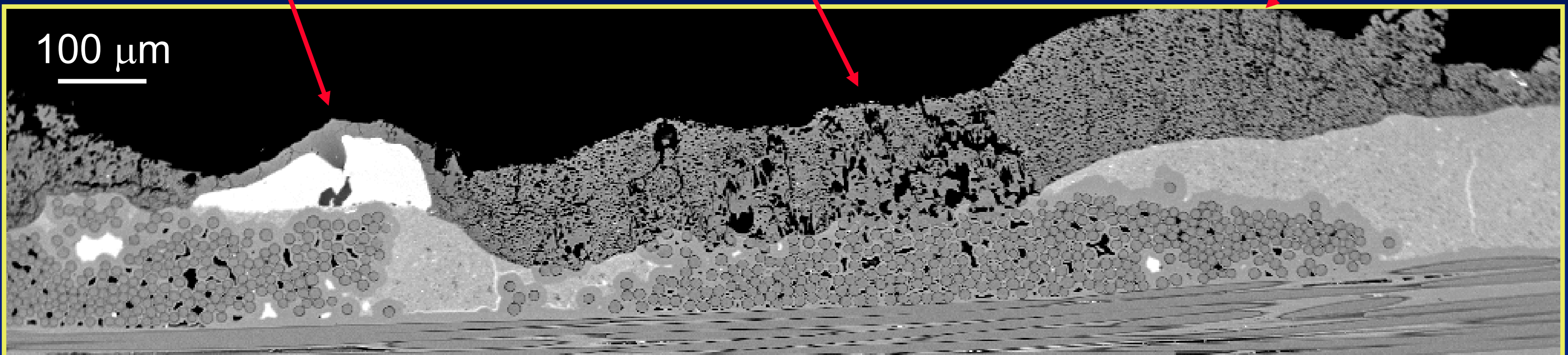


Effects Of Various Constituents On Oxidation Rate And Mode Of Degradation

Modest Oxidation
Silicon

Rapid Attack
fiber + CVI SiC + BN

Faster Reaction
Si + SiC + impurities



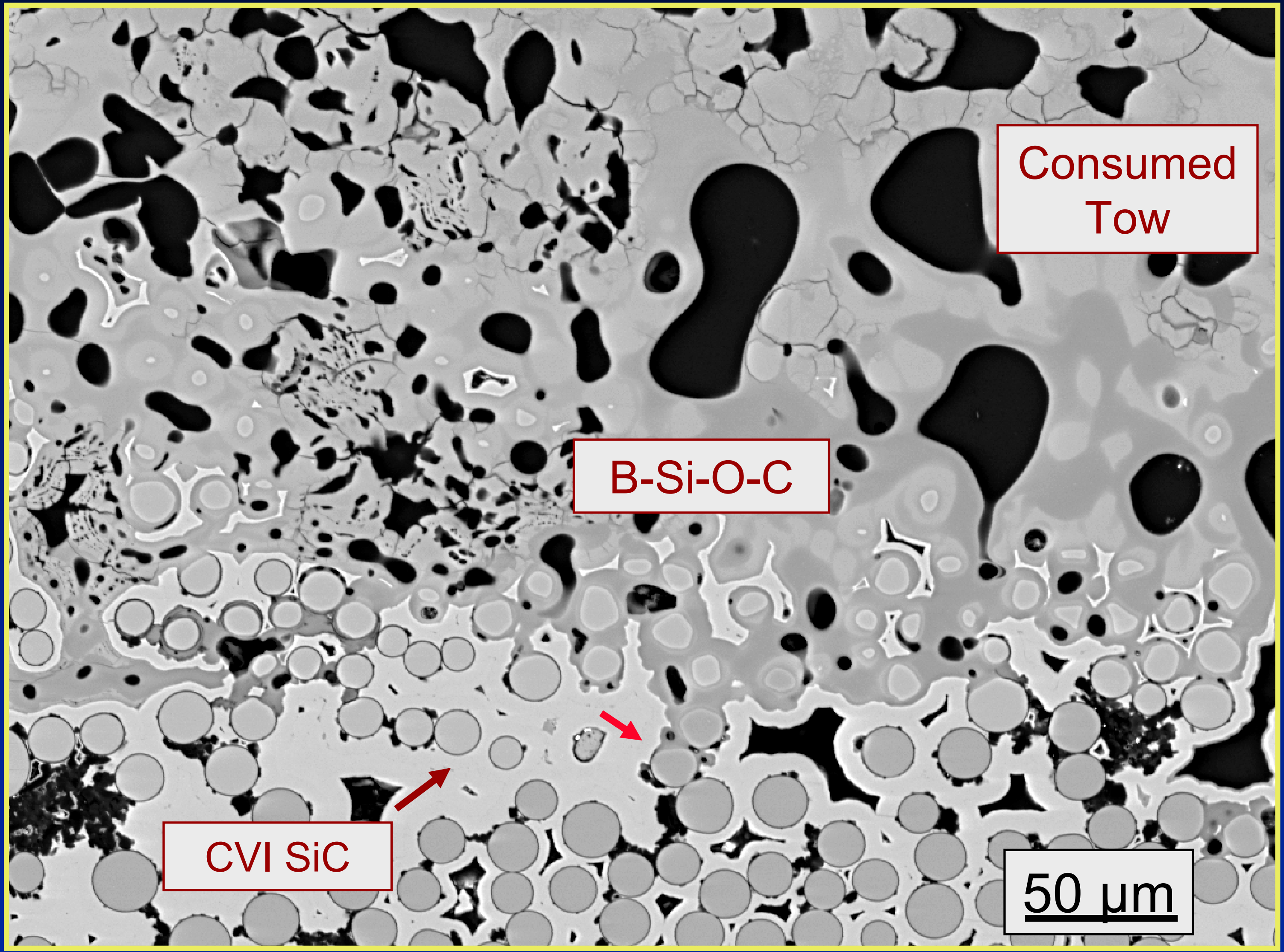
$$Si + 2H_2O\ (g) = SiO_2 + 3H_2\ (g)$$

$$SiC + 3/2O_2\ (g) = SiO_2 + CO\ (g)$$
$$SiC + 3H_2O\ (g) = SiO_2 + CO\ (g) + 3H_2\ (g)$$

$$2BN + 3/2O_2\ (g) = B_2O_3\ (l) + N_2\ (g)$$
$$B_2O_3\ (l) + H_2O\ (g) = 2HBO_2\ (g)$$
$$B_2O_3 + SiO_2 = \text{borosilicate glass}$$

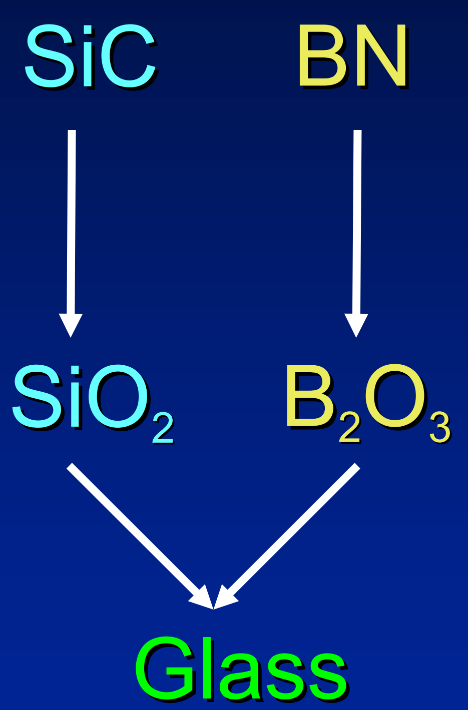
MI SiC/BN/SiC, 1200°C, 500 h, 1.5 atm H_2O

CVI Composite Showed Greater Degradation, But Same Type Of Reactions As MI Composite



1200°C, 1500 h, 1.5 atm H_2O

Composite Degradation Not As Sensitive To Gas Velocity Compared To Monolithic Behavior



$$SiO_2 + H_2O = Si(OH)_4\ (g)$$
$$B_2O_3\ (l) + H_2O\ (g) = 2HBO_2\ (g)$$

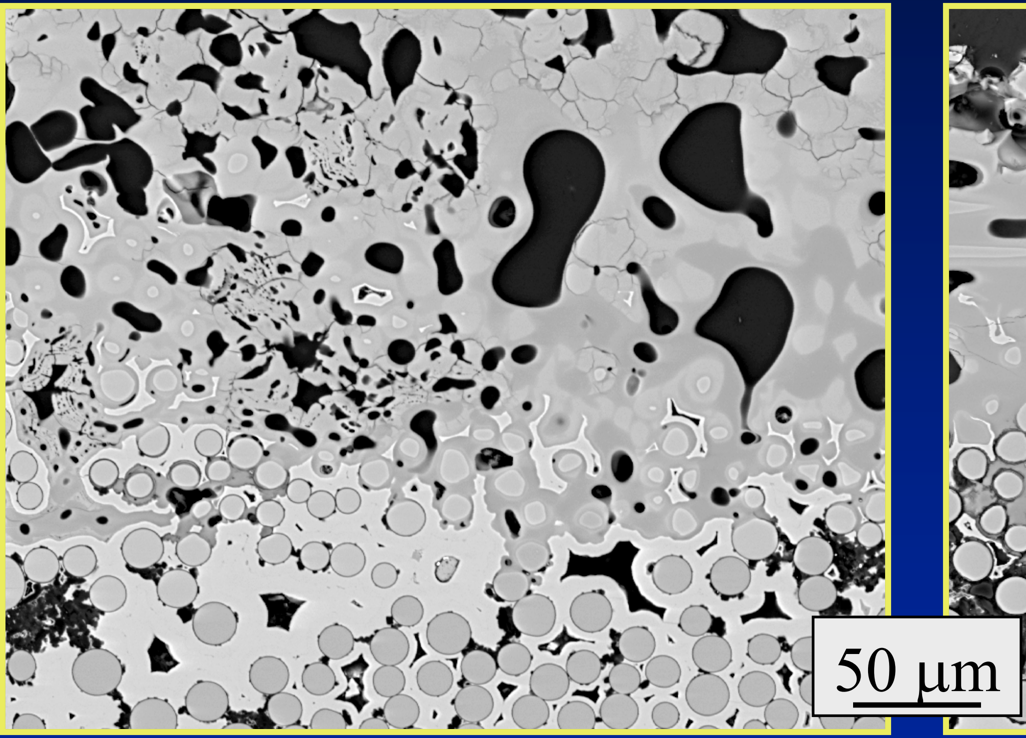
~1200°C, 1.5 atm H_2O

	µm/h
SiC/BN/SiC (~ 30 m/s):	**0.5**
SiC/BN/SiC (~0.05 m/s):	**0.4**

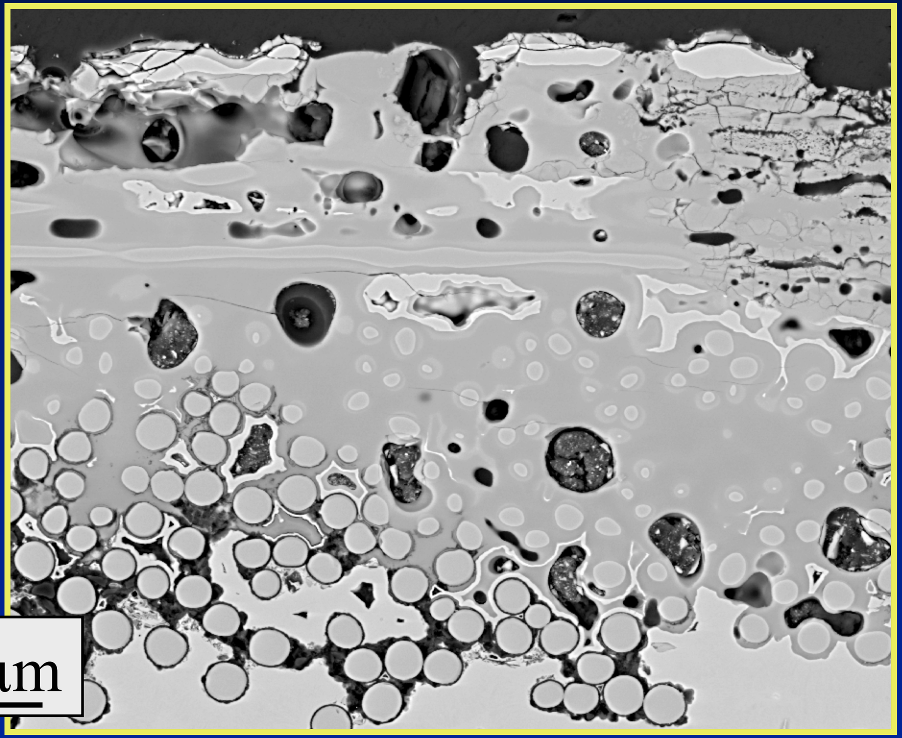
Consistent With Multiple Oxidation Reactions And Borosilicate Glass Formation

Composite Damage Observed In Lab Exposures Was Very Much Like That Of Actual Combustor Liners

Lab Exposure



Engine Test



CVI SiC/BN/SiC, 1200°C, 1.5 atm H_2O

The Keiser Rig Was Used To Expose Uncoated And EBC/CFCCs To Simulated Combustor Conditions

The relevance of the Keiser Rig to the CFCC combustor liner project has been shown by comparing results with similar CFCCs exposed in early Solar Turbines engine tests

- The Keiser Rig exposures (high H_2O pressures, low gas-flow velocities) reproduce the CFCC <u>microstructural damage</u> at an <u>accelerated rate</u> and is comparable to that observed during engine tests

  More, et.al., TurboExpo '99 (ASME pub. #99-GT-292)

  More and Tortorelli, *J. Amer. Cer. Soc.,* (2000)

  More, et. al. Mtls. Science Forum, Vol. **369-72** (2001)

- This test is ideally suited for evaluating damage created <u>below</u> an EBC since velocity is <u>not</u> a factor

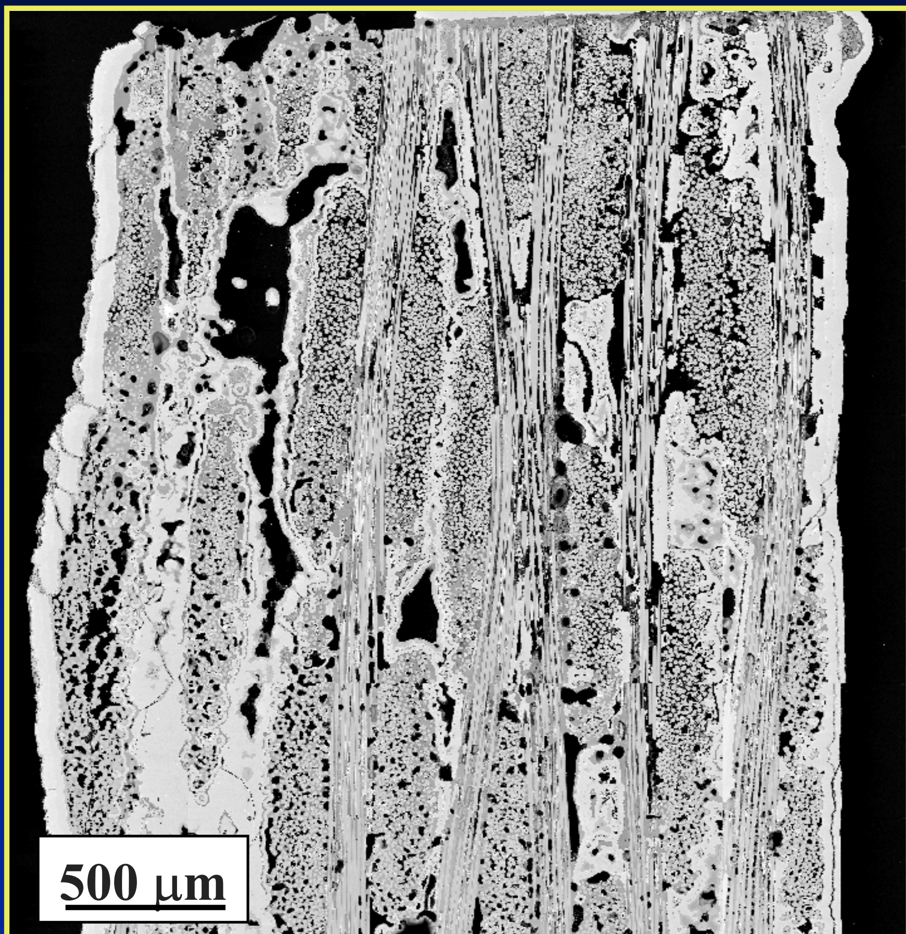
In Order To Reach ~14,000h In Engine, EBCs Were Required For Both CFCC Liners

Without an EBC, the projected <u>lifetimes</u> for SiC seal-coated composite liners are:

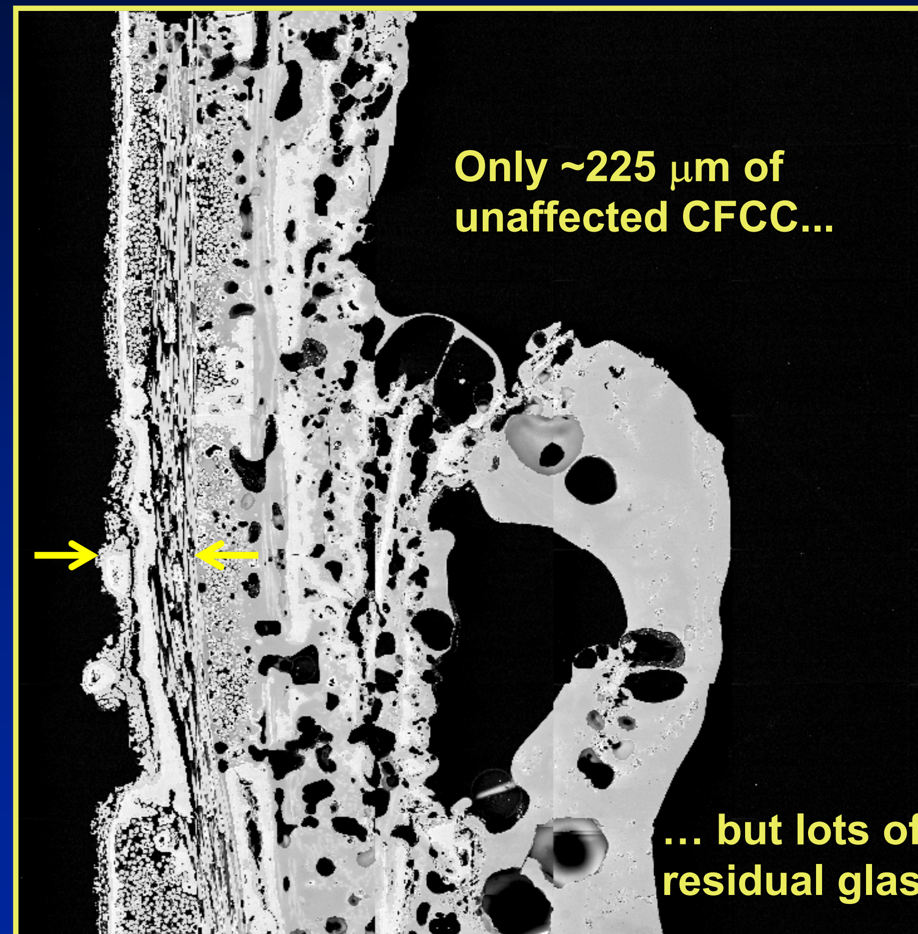
• MI + SiC seal coat (440 μm)	~10,000 h
• Enhanced SiC/SiC + SiC seal coat (520 μm)	~8000 h

(Note: the SiC seal coat thicknesses given here are the same as those on engine-tested liners)

Without An EBC, Significant CFCC Recession And Damage Observed On Surface After Engine Testing



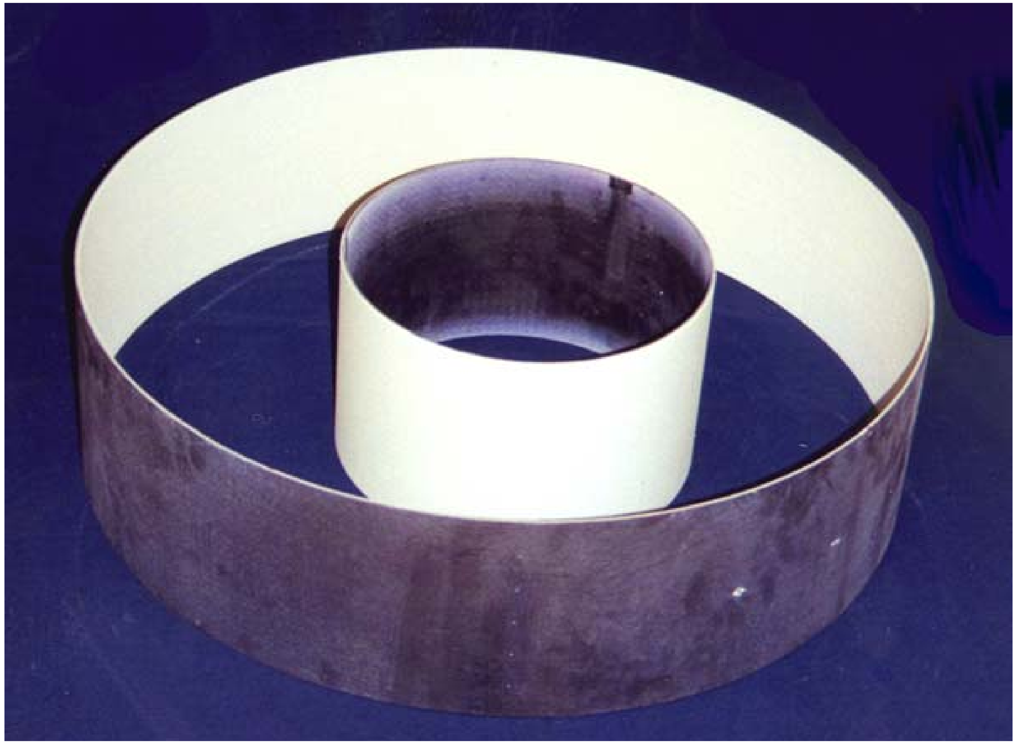
Near top of outer liner



Center of hot spot

EBCs Are Necessary To Increase The Life Of CFCC Combustor Liners

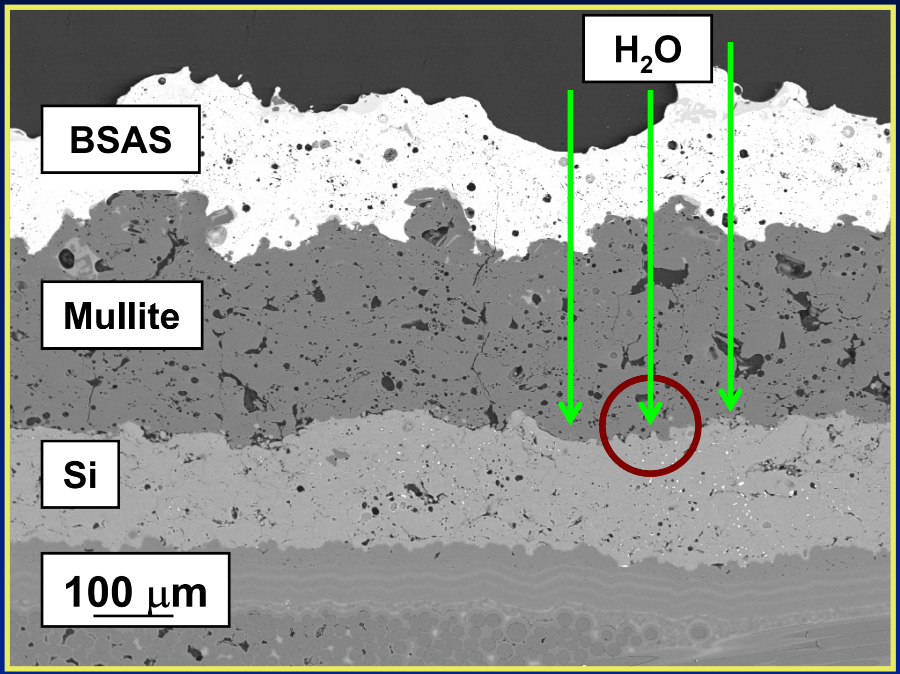
- Protect the CFCC from corrosive environment
  - *EBC must have limited volatility*
  - *EBC must prevent diffusion of O_2 and H_2O*
- Will prevent liner surface recession observed for uncoated CFCC liners
- Will prevent accumulation of sub-surface (CFCC) microstructural damage



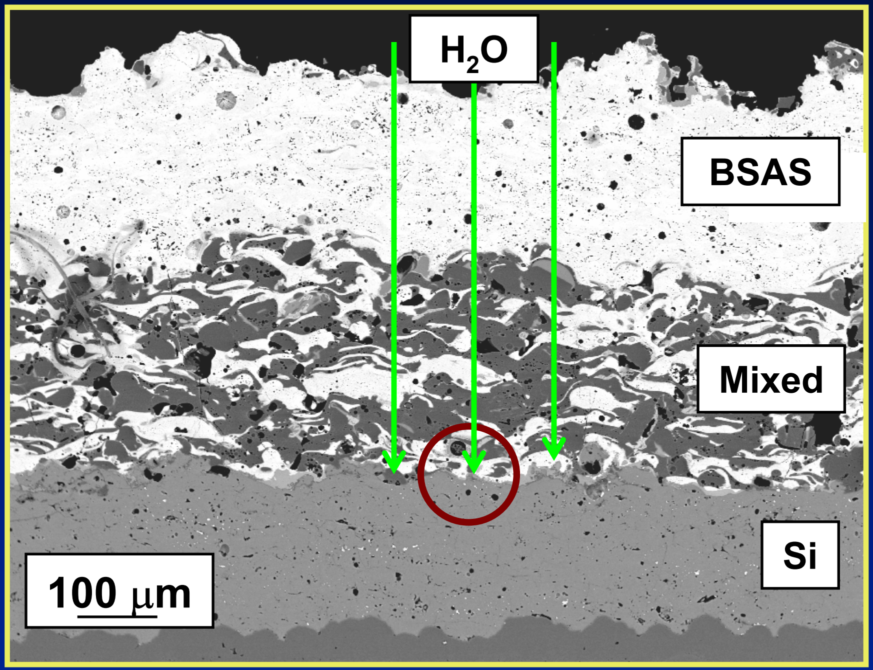
CFCC combustor liners with UTRC EBC on working surfaces which ran ~14,000h at Chevron test site

Two Different Coating Concepts Were Exposed Simultaneously In The Keiser Rig And In Engine Tests

Plasma sprayed coatings consist of two oxide layers on a Si bond coat and CVD SiC seal coat



"Dual layer" Mullite/BSAS
Inner Liner at Chevron



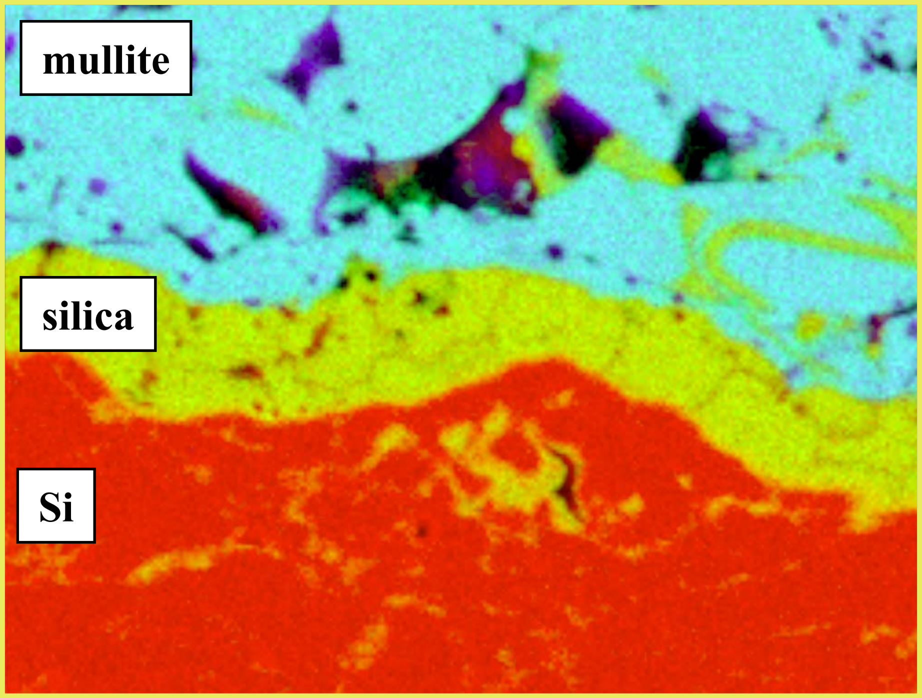
"Mixed layer" (Mullite+BSAS)/BSAS
Outer Liner at ChevronLiner set at Malden Mills

The Keiser Rig can be used to effectively evaluate:

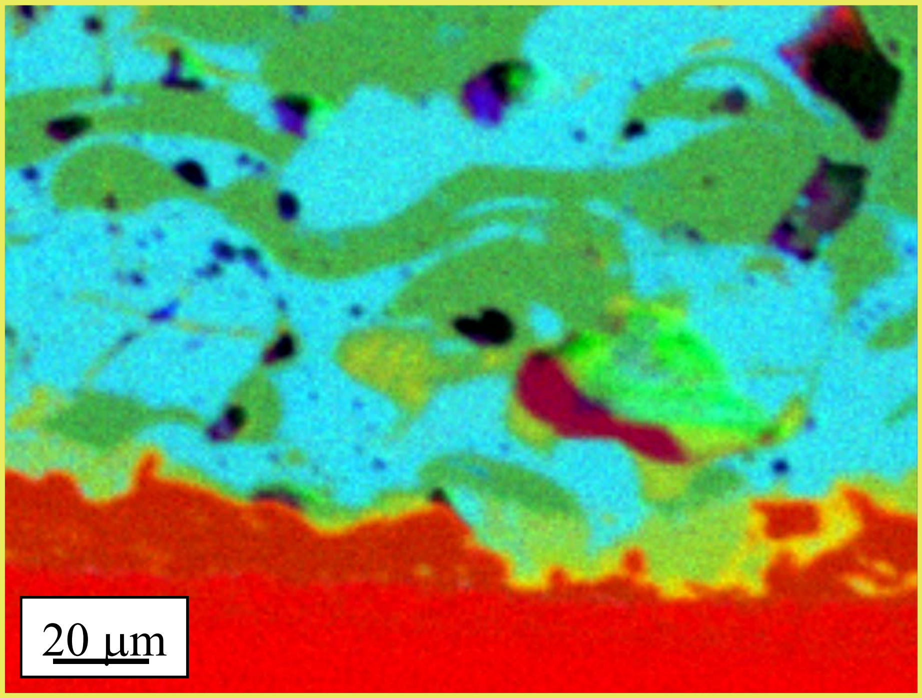
- *the protective capability of different EBCs*
- *the thermal stability of EBC constituents*

Differences Were Observed In Silica Layer Formed Within "Dual" And "Mixed" Layer EBCs

Comparison after 1500 h exposure @ 1200°C in Keiser Rig

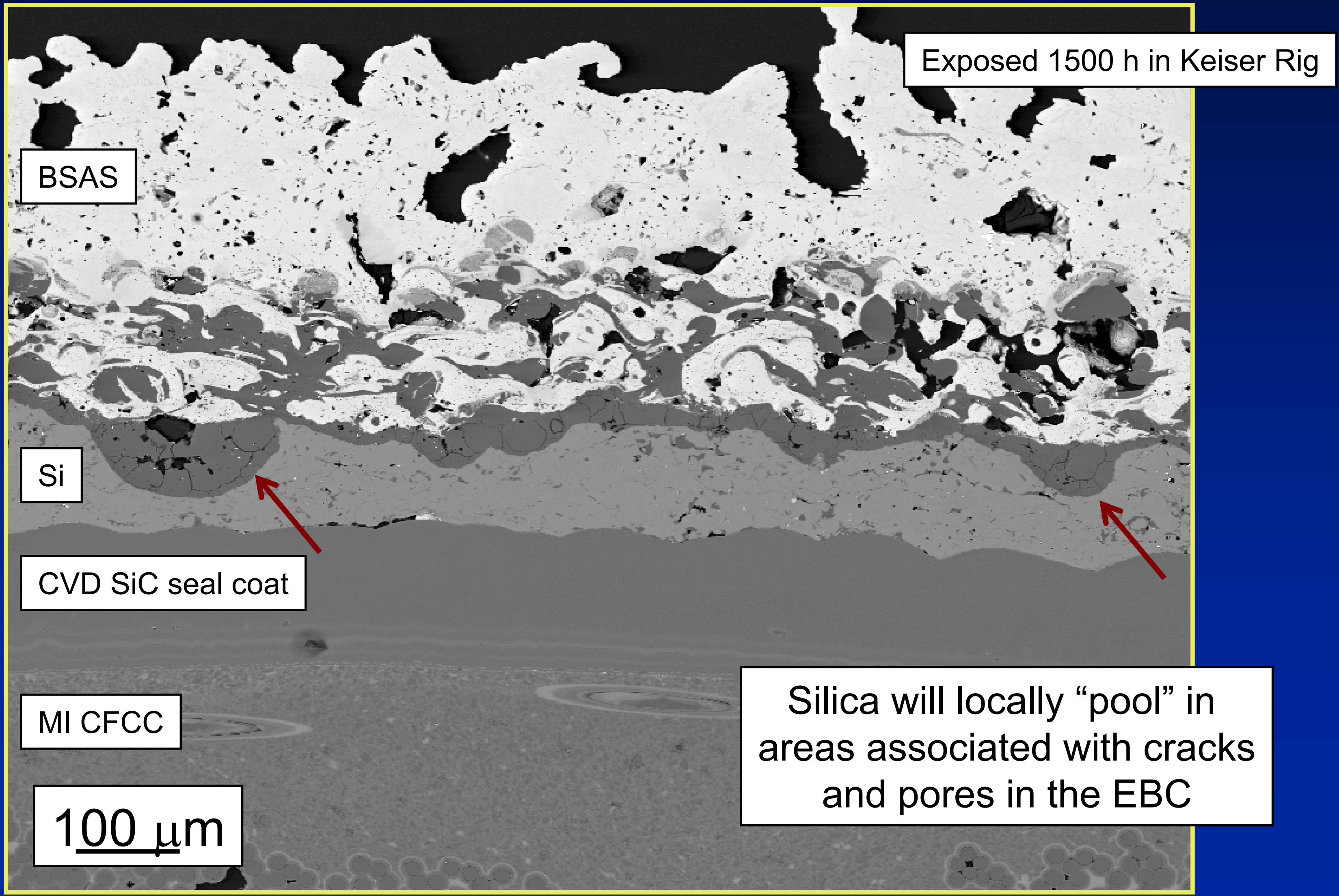


"Dual layer" Mullite/BSAS



"Mixed layer" (Mullite+BSAS)/BSAS

Processing Defects Play A Critical Role In The Effectiveness Of EBCs

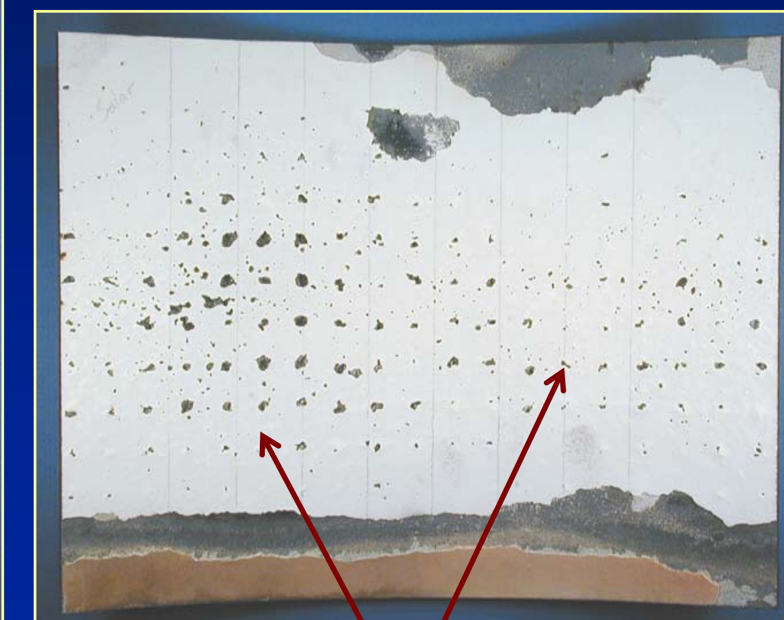


Evaluation Of Many Sections Of ~14,000h Liner Set Revealed Three Primary Degradation Modes

- BSAS recession/volatility in combustor environments
- The stability of mullite in combustor environments
- The contribution of tool bumps to EBC spallation

Recession/volatilization of BSAS exposing CFCC

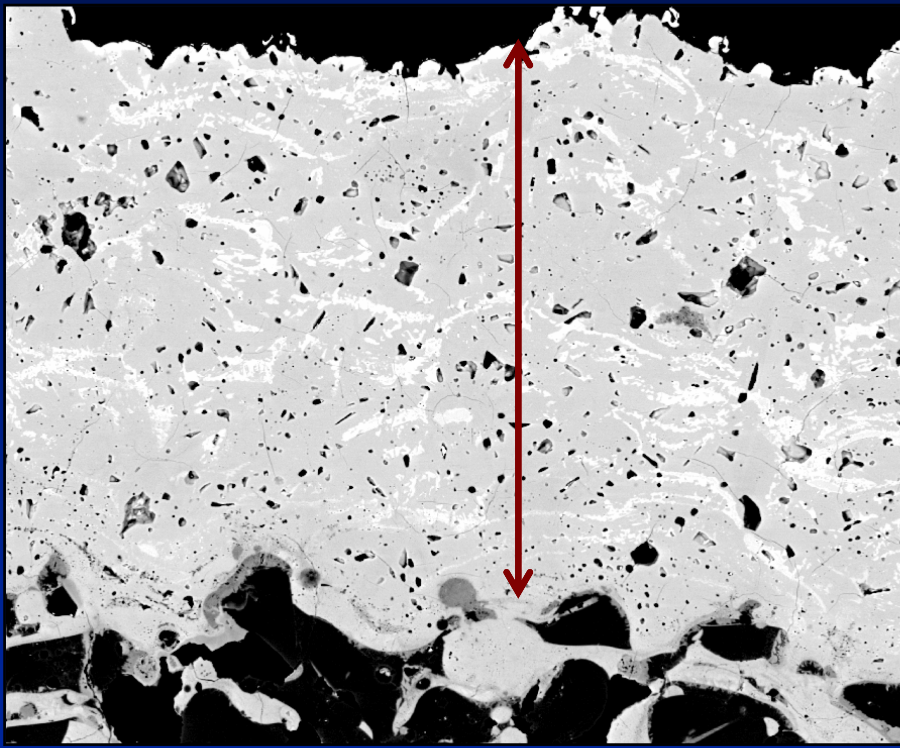
Recession/volatilization of BSAS exposing SiC seal coat and other EBC layers



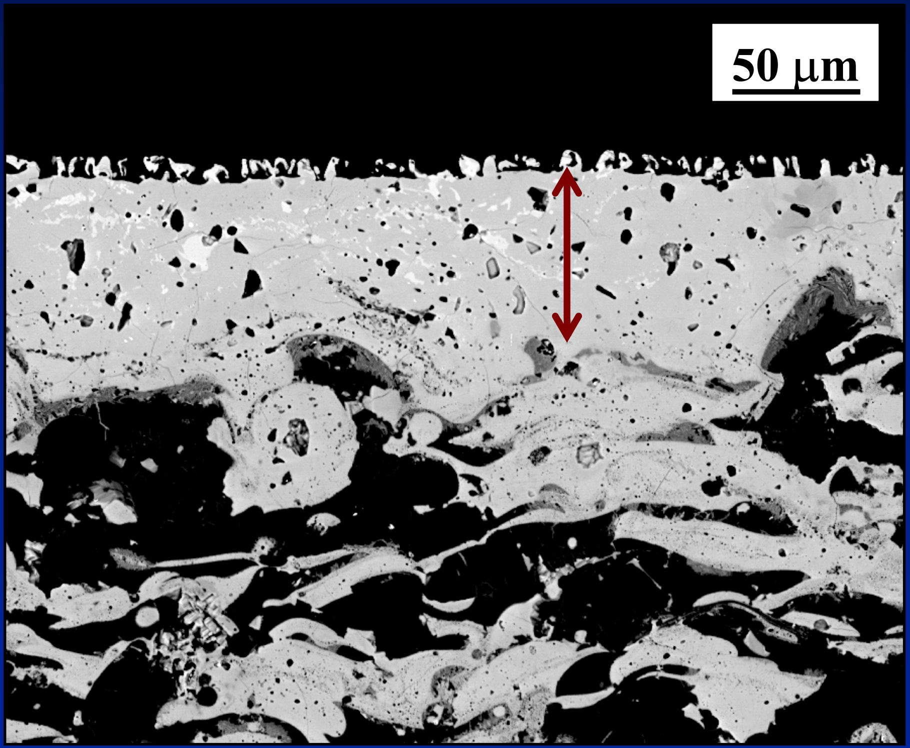
Pinholes associated with CVI tooling pattern

BSAS Recession Was Observed Regardless Of Type Of EBC (Dual vs. Mixed)

Definite (but unexpected?) volatility issue associated with the BSAS



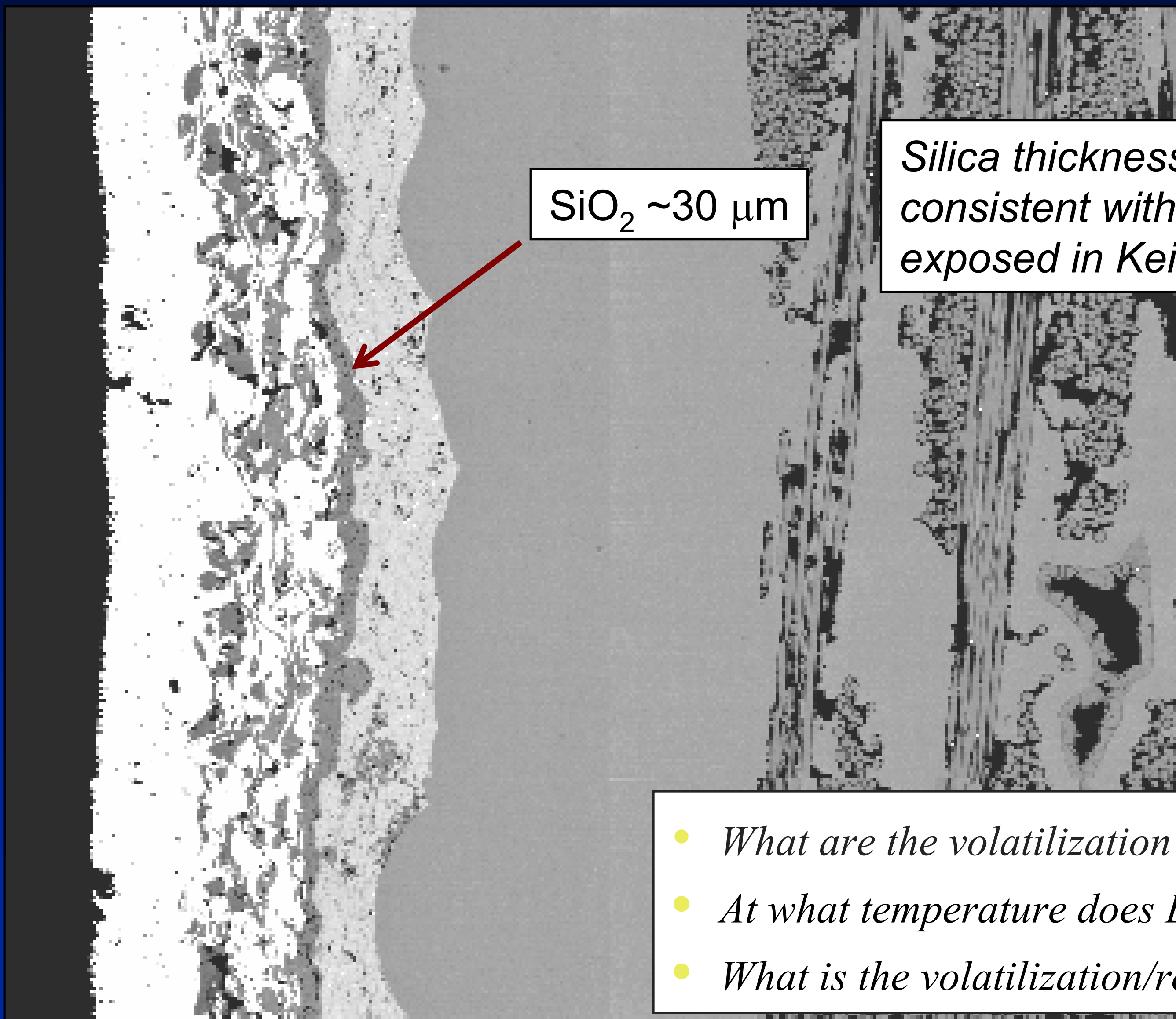
Aft



Middle

Outer liner section with mixed-layer EBC

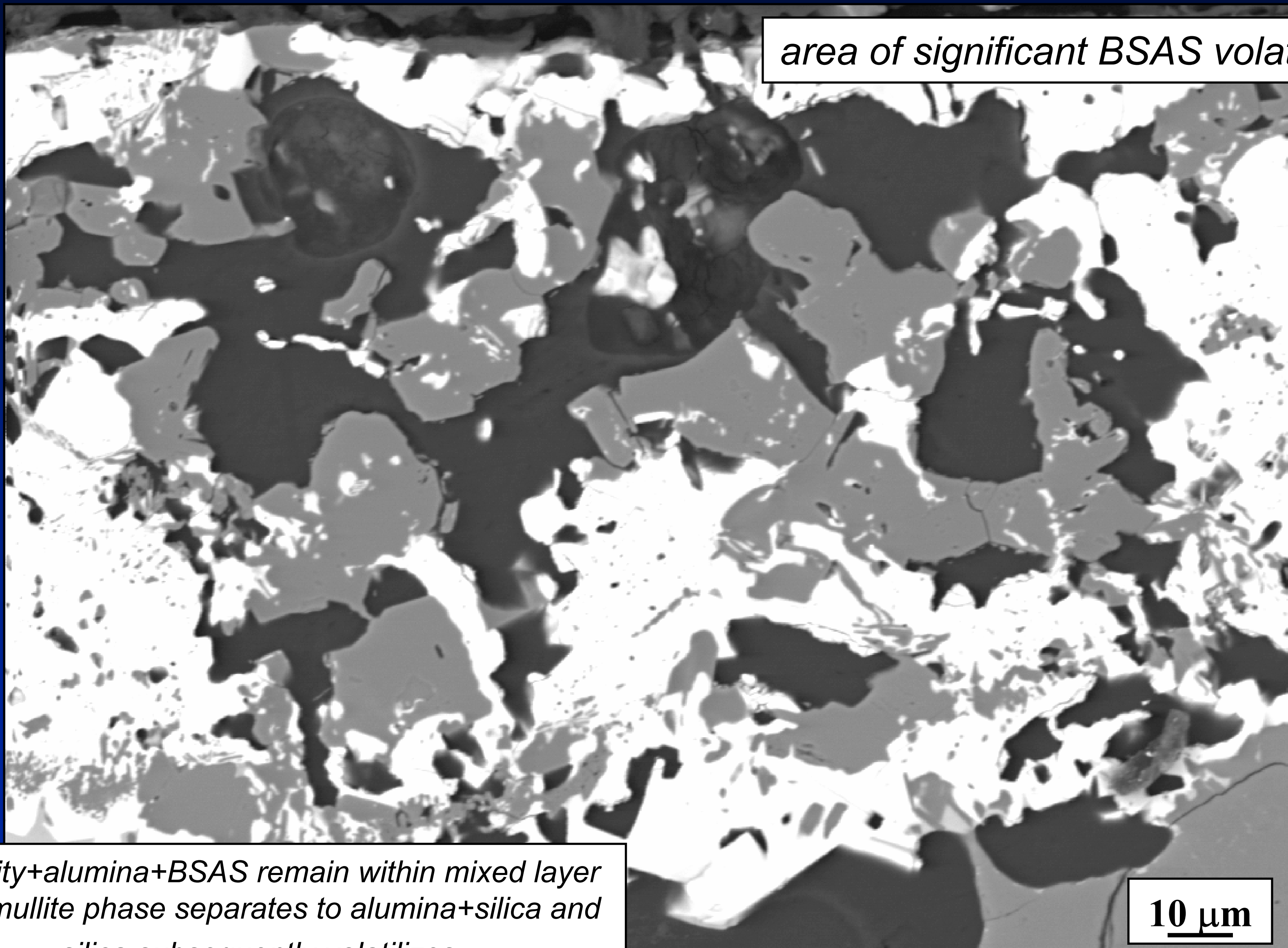
The Mixed-Layer EBC Is Still Protective In Well-Processed Areas Even After Some BSAS Recession



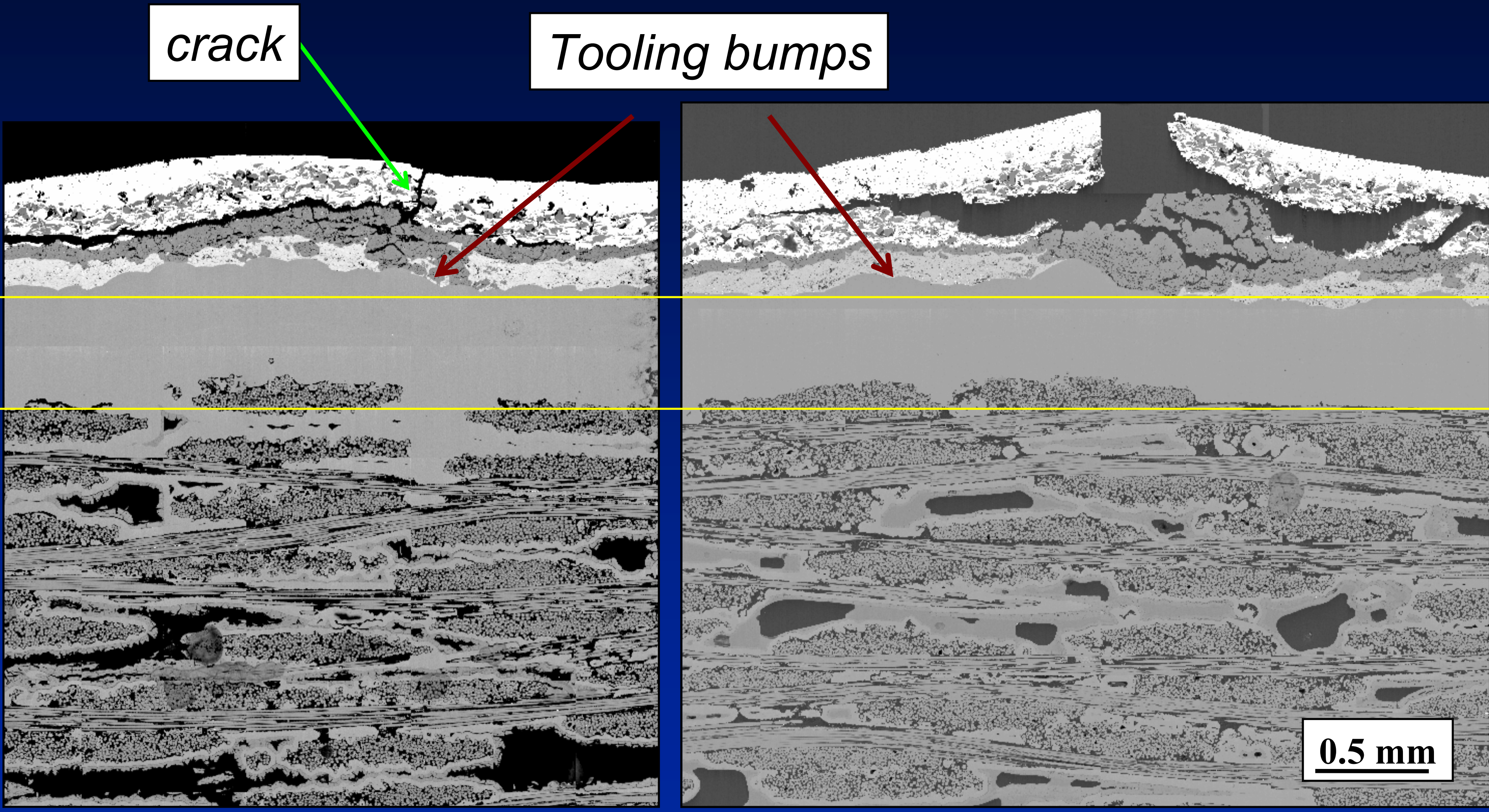
Silica thickness after ~14,000h is consistent with that found in samples exposed in Keiser Rig for 6500h

- *What are the volatilization mechanisms for BSAS?*
- *At what temperature does BSAS volatilization start?*
- *What is the volatilization/recession rate for BSAS?*

In Areas Where BSAS Top Coat Has Fully Recessed, Exposed Mullite Degrades Rapidly

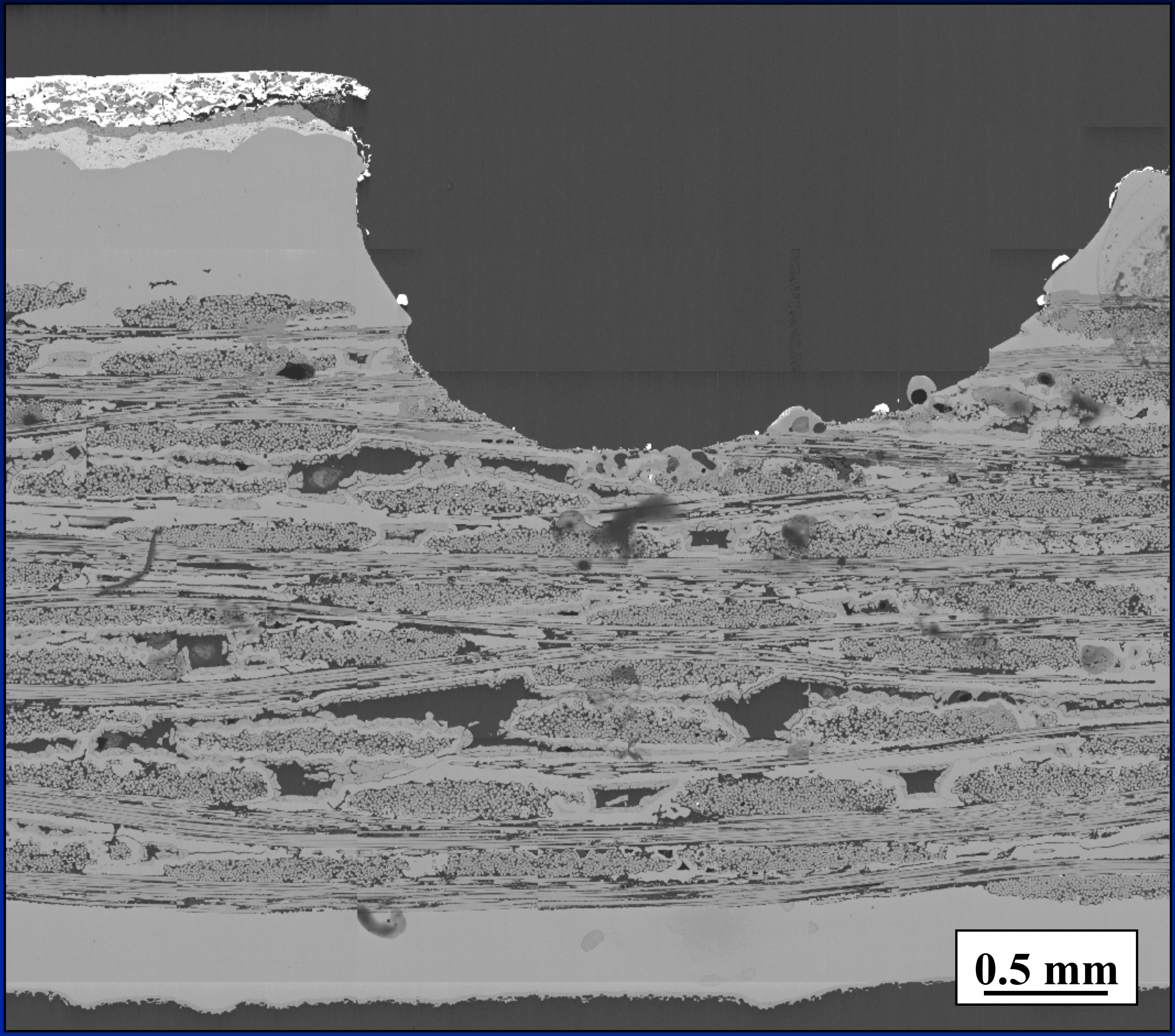


Tool Bump Areas Showing Early Stages Of EBC Spallation In Cooler Sections Of Outer Liner



The as-processed EBCs generally have a through-thickness crack associated with the tool bumps (or any other surface asperity)

Typical Cross-Section Through Pinhole On Surface Of Outer Liner Shows Accelerated Oxidation Of CFCC



Future Directions

- EBCs will be necessary to prevent surface recession and subsurface microstructural damage of CFCC combustor liners. However, BSAS recession and mullite stability must be addressed to increase life
- ORNL's Keiser Rig is an effective way to screen improved EBC formulations under simulated combustor conditions (i.e. high H_2O pressures)
- Additional liner sets will be characterized (Malden Mills, Chevron) in order to provide additional information on new CFCC and EBC formulations
- Knowledge and experience gained from this program should be extremely useful for defining CFCC and ceramic applications/components in microturbines